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FOAM GLASS AND POLYMER MATERIALS: EFFECTIVE OIL SORBENTS

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Foam glass and glassy materials (polyurethanes) are studied for use as oil sorbents. The specific character of the kinetic curves of oil absorption determined by the glassy state of the surface irrespective of its nature (inorganic or organic) is determined. Promising practical applications of the results obtained are found.

Key words: glass, glassy state, oil sorbents, kinetics of oil absorption, polymers.

The most harmful environmental pollutants are oil and oil products. Active production of ever larger quantities of oil has been ongoing for more than 100 years. As a result the magnitude of the contamination occurring in regular situations is becoming larger with the most dangerous accidents in terms of scale and consequences occurring during shipment by sea.

The methods used to clean up water surfaces contaminated by oil and oil products can be divided into four main groups: mechanical methods, performed using all possible contrivances for collecting the oil; physical-chemical methods, based on physical-chemical phenomena; biological methods, implemented using microbiological cultures; and, photochemical, occurring under the action of sunlight and catalysts. The physical-chemical methods are the ones most commonly used, the sorption based methods being preeminent.

In spite of the large amount of research on the development of oil sorbents, the problem of cleaning up contamination by oil and oil products cannot be considered as solved. In our view there are two reasons for this. The first one is that the overwhelming majority of this work is focused on the development of oil sorbents for practical use rather than for determining the physical-chemical mechanisms of oil absorption on them, which would make it possible to develop the scientific principles for obtaining oil sorbents with a prescribed set of physical-chemical processes and working parameters. The second reason is that the assortment of materials for obtaining oil sorbents is too narrow.

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Among the least studied materials in terms of the present investigations is foam glass — a unique material, entirely comprised of glass cells, developed in the 1930s in the USSR (D. I. Mendeleev Moscow Chemical Technology Institute) and in the 1940s in the USA (Corning Glass Works). This sounds somewhat paradoxical, since it was initially proposed that foam glass be used as a buoyant material, and buoyancy is one of the required properties of oil sorbents.

Of all foam glasses produced by industry we settled on a foam glass manufactured by Gomel'steklo JSC. This is because hard coal is used in the production of the foam glass. The glass obtained without disrupting the technological regime is black, indicating that carbon residues, whose hydrophobic and adsorption properties are well known, remain on the surface of the glass [1].

REBCO oil (Russian Export Blend Crude Oil) was used in the present work. This is an exported oil blend, formed in the 'Transneft' system of pipelines by mixing a heavy high-sulfur oil from Ural-Povolozh'e and low-sulfur oil from Western Siberia, whose properties correspond to those of Urals brand oil.

Heat-treatment in a silane solution was used to hydrophobize foam glass samples (3 – 8 mm fraction). The oil absorption, water absorption and buoyancy were determined following TU 124-10942238-03–95 'Determination of sorbent efficiency' [2].

The water absorption of the hydrophobized samples was zero. The buoyancy of all samples (hydrophobized and not hydrophobized) has now lasted for 4 months; this is also true for samples which have reached maximum saturation with oil. No oil desorption from the samples in time is observed.

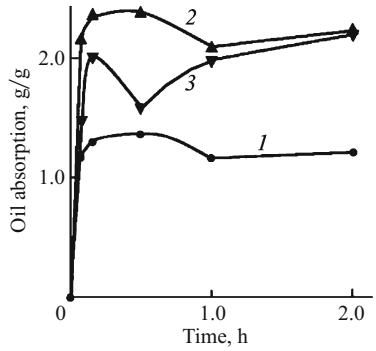

Fig. 1. Kinetics of absorption by foam-glass sorbents: *1*) hydrophobized; *2*) foam glass without hydrophobization; *3*) yellow foam glass (oxidation of coal) without hydrophobization.

The investigation of oil absorption produced the most interesting results (Table 1, Fig. 1).

If the kinetic curves for all known oil sorbents (see, for example, [3 – 5]) are characterized by an increase of oil absorption followed by saturation, then the absorption kinetics of our foam glasses is initially characterized by the presence of a maximum. Such dependences have not been published in the literature.

The kinetic curve for both hydrophobized and non-hydrophobized foam glasses exhibits a maximum at 30 min. It is known [6] that for silicate materials, such as the foam glasses studied here, a very common process of mass transport of a liquid in a porous body is capillary permeation made possible by capillary forces. This is probably happens in our case.

The best way to proceed is to correlate the drop observed in the oil absorption after the completion of this process and the processes accompanied by gas release. In this case the pressure of the gaseous products formed is sufficient to displace some oil from the pores. We associate the greater oil absorption in non-hydrophobized samples with the inhibiting

TABLE 1. Kinetics of Oil Absorption by Foam-Glass Sorbents

Oil contact time	Oil absorption by foam glass, g/g		
	hydrophobized*	no hydrophobization*	no hydrophobization**
5 min	1.17	2.16	1.47
10 min	1.30	2.36	2.03
30 min	1.36	2.38	1.59
1 h	1.16	2.10	1.98
2 h	1.21	2.25	2.20
12 h	1.31	2.47	–
24 h	1.54	2.47	–
48 h	1.54	2.47	–

* Black foam glass

** Yellow foam glass (oxidation of coal).

effect of the hydrophobizer on the adsorption properties of the residual carbon localized on the surface of the glass. The fragments of the hydrocarbon chains of the hydrophobizer form a layer of appreciable thickness, which is what leads to a reduction of the specific surface area of the sorbent as a result of the closure of small pores. Indeed, the specific surface area of hydrophobized samples (as determined by the Klyachko–Gurvich method) is smaller by 1.6 m^2/g.

To check the inhibiting effect of the hydrophobizer on the adsorption properties of residual carbon localized on a glass surface we studied the kinetic curve of oil absorption for a foam-glass sample obtained with a disruption of the process regime (see Fig. 1). The yellow color of the sample attests to a sharp reduction of the content of residual carbon on the glass surface. Indeed, an elemental analysis performed with a Vario EL CHN-analyzer (Germany) showed that the carbon content on the sample does not exceed 0.45%, while for the black sample it reached 0.87%. The oil absorption of the yellow sample is greater than that of hydrophobized glass but lower than of the black sample without hydrophobization. This confirms the presence of adsorption by residual carbon on the surface of glass and the inhibiting effect of a hydrophobizer on adsorption. The elemental analysis has shown a high content of carbon in the hydrophobized sample, reaching 8.84%. However, it should be understood that this occurs not because of an increase in the content of residual carbon localized on the glass surface but rather because carbon is imported together with fragments of hydrocarbon chains of the hydrophobizer. This is supported by the fact that the elemental analysis also shows that the hydrogen content in the hydrophobized foam glass increases to 2.77%, while in foam glass without hydrophobization it does not exceed 0.26%. The shift of the oil absorption peak by 10 min in the yellow foam glass is due to an increase of the capillary permeation rate as a result of an increase in the radius of the capillaries.

On this basis it can be supposed that the character of the dependences obtained is due to the particulars of the glassy state. To check this we studied a sample of foam glass obtained under laboratory conditions without using coal (Fig. 2) and without hydrophobization.

The kinetic curve of the density obtained correlates with the kinetic curves presented in Fig. 1. This shows unequivocally that the assumption made is valid. The shift in the peak by 45 min is due to the readily observed reduction of the capillary radius, which results in a reduction of the rate of capillary permeation.

This investigation of the kinetics of oil absorption by foam-glass sorbents raised the following question: is the character of their kinetic curves of oil absorption a result of the characteristics of the inorganic glassy state (particulars of silicate glasses) or is it inherent to any glassy state? An investigation using organic polymer materials (solid polyurethane foams), which are well known to be capable of existing

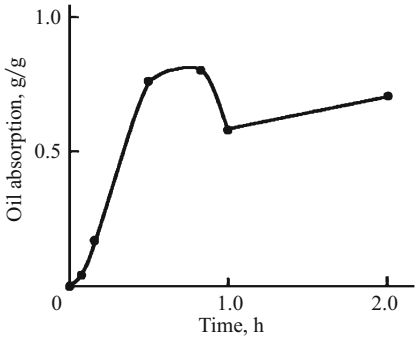

Fig. 2. Oil absorption kinetics of a laboratory sample of foam glass obtained without hydrophobization or the use of coal.

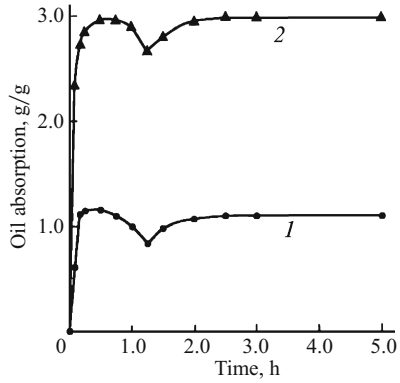

Fig. 3. Kinetics of oil absorption by PUF-Piter sorbents.

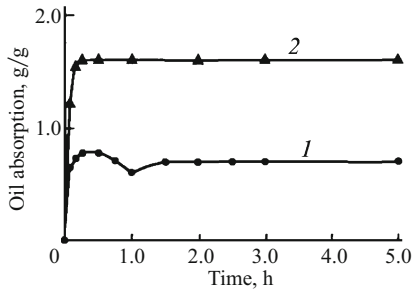

Fig. 4. Kinetics of oil absorption by PUF-Minsk sorbent.

in the glassy and crystalline states, was performed to answer this question.

In contrast to ordinary crystalline solids, crystalline polymers do not consist of some crystals. For polymers even the concept of 'crystals' differs somewhat from the standard one. In crystalline polymers there are regions (zones) where individual sections of macromolecules have close-packing reminiscent of rhombic plates (distinctive crystals). These regions co-exist with the main amorphous (glassy) polymer mass. Thus, the glassy (in terms of the amorphous state of polymers, we are studying only the glassy state) and crystalline parts consist of identical macromolecules, but in the glassy part they are arranged in a disordered fashion while in the crystalline part they are closely packed because of the ordered arrangement.

Although most polymers are amorphous substances they differ by the presence of some crystallinity, confirmed by x-ray studies. The crystallized volume fraction can reach 80%. In the present work, when speaking about the crystalline or glassy state of polymer foams we mean the state of their surface first and foremost.

On this basis, for the objects of study we chose two types of solid (rigid) polyurethane foams (PUF): a glassy PUF produced by Poliprom JSC in St. Petersburg (PUF-Piter) and used as construction thermal insulation and a crystalline PUF produced by the Belorussian-American joint venture company TSIN EAST TRADE JSC in Minsk (PUF-Minsk) and marketed by the company as a cosmetic pumice. Both experimental objects are PUFs with a closed cellular structure.

The water absorption of the hydrophobized polyurethane foam samples was close to zero. The buoyancy of all hydrophobized and non-hydrophobized samples has now exceeded 4 months, and this is also the case for samples fully saturated with oil.

The investigation of oil absorption yielded the most interesting results (Table 2, Figs. 3 and 4).

The PUF-Piter samples (hydrophobized and not hydrophobized) exhibit kinetic curves of absorption similar to the ones we obtained for foam-glass oil sorbents. The kinetic curve peaks in the range 30 – 45 min for the sample without hydrophobization and 15 – 30 min range for the hydrophobized sample.

In our view these peaks (see Table 2 and Fig. 3) are present for the same reasons as in the case of foam-glass oil

TABLE 2. Kinetics of Oil Absorption by Polyurethane Foam Sorbents

Duration of contact with oil	Oil absorption by sorbent, g/g			
	PUF-Piter		PUF-Minsk	
	without hydrophobization	hydrophobized	without hydrophobization	hydrophobized
5 min	2.35	0.62	1.22	0.65
10 min	2.73	1.12	1.56	0.72
15 min	2.86	1.15	1.61	0.78
30 min	2.96	1.16	1.61	0.78
45 min	2.96	1.10	–	0.71
1 h	2.90	1.00	1.61	0.61
1 h 15 min	2.67	0.84	–	–
1 h 30 min	2.81	0.98	–	0.70
2 h	2.96	1.07	1.61	0.70
2 h 30 min	3.00	1.10	1.61	0.70
3 h	3.00	1.10	1.61	0.70
5 h	3.00	1.10	1.61	0.70

sorbents. Indeed, it is well known [6] that for porous polymer materials, just as for silicate materials, a common process of liquid mass transport in porous bodies is capillary permeation due to capillary forces. Probably it occurs in the present case also.

The drop in oil absorption observed after the completion of this process correlates best with the process accompanying gas release. In this case the pressure formed by gaseous products is adequate for displacing a portion of the oil from pores. We correlate the higher oil absorption in samples not subjected to hydrophobization with two factors. In the first place, as in the case of foam glasses, fragments of hydrocarbon chains of the hydrophobizer form a layer of appreciable thickness, which simultaneously also results in a reduction of the specific surface area of the sorbent as a result of the closure of small pores. In the second place, our hydrophobization procedure included a thermal stage, after which the samples were observed to shrink (volume reduction). At the same time it is known [7] that when oil interacts with absorbers having a closed-cellular structure it penetrates into the porosity space of the sorbent layer. In the present case the volume of this space decreased as a result of hydrophobization.

In summary, the investigation of only the PUF-Piter oil sorbent already has shown that the specific character of the kinetic curves of oil absorption is due to the glassy state of the surface irrespective of its nature (inorganic or organic).

The results of the investigation of the absorption kinetics of the PUF-Minsk sorbent (see Table 2, Fig. 4) comprise the final confirmation of the conclusion formulated above. Indeed, for the PUF-Minsk crystal sample without hybridization the kinetic curve of oil absorption is identical to the curves obtained for all known sorbents (see, for example, [3 – 5]), for which the kinetic curves are characterized by an increase of the oil absorption followed by saturation. At the same time the hydrophobized PUF-Minsk sample exhibits a kinetic curve of oil absorption similar to glasses and glassy materials: it is characterized by the presence of a peak in the range 15 – 30 min. In our view this is due to the already observed thermal stage of the process of hydrophobization, whose temperature reached a value of the order of 330 K, while the vitrification temperature of polyurethanes is 226 – 356 K. Thus, we can say that in the hydrophobization process a transition occurred from a crystalline into a glassy state, and the rate of the subsequent cooling was adequate for this state to persist.

The results of this investigation, including those of a theoretical nature, showed the practical import of this work.

CONCLUSIONS

The materials investigated can be recommended for containing accidental oil spills (manufacture of booms) and for removing films from the surface of water.

The character of the kinetic curves of oil absorption could provide a basis for an indirect method of determining the state of the sorbent (glassy or crystalline).

The state of the surface of polymer sorbents can change (from crystalline to glassy).

In choosing a hydrophobizer and a method of hydrophobization it is necessary to maintain at least the specific surface area of the initial material and to prevent the inhibiting effect of the hydrophobizer on the adsorption capacity of the surface.

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